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**the Science of the
Total Environment**

An International Journal for Scientific Research
into the Environment and its Relationship with Man

The Science of the Total Environment 260 (2000) 57–71

www.elsevier.com/locate/scitotenv

Mercury mine drainage and processes that control its environmental impact

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Received 27 September 1999; accepted 31 March 2000

Abstract

Mine drainage from mercury mines in the California Coast Range mercury mineral belt is an environmental concern because of its acidity and high sulfate, mercury, and methylmercury concentrations. Two types of mercury deposits are present in the mineral belt, silica-carbonate and hot-spring type. Mine drainage is associated with both deposit types but more commonly with the silica-carbonate type because of the extensive underground workings present at these mines. Mercury ores consisting primarily of cinnabar were processed in rotary furnaces and retorts and elemental mercury recovered from condensing systems. During the roasting process mercury phases more soluble than cinnabar are formed and concentrated in the mine tailings, commonly termed calcines. Differences in mineralogy and trace metal geochemistry between the two deposit types are reflected in mine drainage composition. Silica-carbonate type deposits have higher iron sulfide content than hot-spring type deposits and mine drainage from these deposits may have extreme acidity and very high concentrations of iron and sulfate. Mercury and methylmercury concentrations in mine drainage are relatively low at the point of discharge from mine workings. The concentration of both mercury species increases significantly in mine drainage that flows through and reacts with calcines. The soluble mercury phases in the calcines are dissolved and sulfate is added such that methylation of mercury by sulfate reducing bacteria is enhanced in calcines that are saturated with mine drainage. Where mercury mine drainage enters and first mixes with stream water, the addition of high concentrations of mercury and sulfate generates a favorable environment for methylation of mercury. Mixing of oxygenated stream water with mine drainage causes oxidation of dissolved iron(II) and precipitation of iron oxyhydroxide that accumulates in the

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streambed. Both mercury and methylmercury are strongly adsorbed onto iron oxyhydroxide over the pH range of 3.2–7.1 in streams impacted by mine drainage. The dissolved fraction of both mercury species is depleted and concentrated in iron oxyhydroxide such that the amount of iron oxyhydroxide in the water column reflects the concentration of mercury species. In streams impacted by mine drainage, mercury and methylmercury are transported and adsorbed onto particulate phases. During periods of low stream flow, fine-grained iron hydroxide sediment accumulates in the bed load of the stream and adsorbs mercury and methylmercury such that both forms of mercury become highly enriched in the iron oxyhydroxide sediment. During high-flow events, mercury- and methylmercury-enriched iron hydroxide sediment is transported into larger aquatic systems producing a high flux of bioavailable mercury. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords Mercury; Mine, Mine drainage; Adsorption, Methylmercury, Mine tailings

1. Introduction

Mercury mines pose an environmental concern because of the presence of mine tailings commonly termed calcines, and waste rock that contribute mercury-enriched sediment to watersheds. At some mines, mine drainage that is often acidic and that contains elevated levels of mercury and other toxic metals also impacts water quality and biota. Remediation measures implemented at mercury mines have primarily addressed the release and transport of mercury from calcines and waste rock by controlling erosion through slope stabilization and re-vegetation (Whyte, 1998). The environmental impact of mine drainage is presently being assessed at several mines but successful remediation measures have as yet to be identified and implemented.

This paper presents information on the composition of mercury mine drainage from several mercury mines in the California Coast Range mercury mineral belt. Streams impacted by mercury mine drainage have been shown to be favorable environments for methylation of mercury (Rytuba, 1997; Rytuba and Enderlin, 1999). Mercury contaminated soils, including mine wastes, can also be favorable sites for methylation (Hines et al., 1999). The processes that control mercury and methylmercury concentration and transport in mine drainage and streams impacted by mine drainage are described in this paper.

2. Sampling and analytical procedures

Sampling was carried out under stable weather

conditions with no precipitation. The pH, was measured at sample sites with an Orion model 250 pH meter using an Orion Ross Sure-Flow electrode. Samples for anions and cations were filtered at the site through a 0.45- μ m membrane filter. Samples for anion analysis were collected into high-density polyethylene bottles. Samples for iron analysis were collected in opaque bottles and acidified with ultrapure reagent-grade Ultrex hydrochloric acid to pH < 2. The samples were stored in an ice chest and later in a refrigerator and kept cool until analyzed. Sulfate concentrations were determined by ion chromatography (Fishman and Pyen, 1979). Total iron was analyzed by inductively coupled plasma mass spectrometry (ICP-MS), and Fe(II) by colorimetric methods in USGS laboratories. Duplicate water samples, blank samples, and USGS Water Resource Division standard reference waters were analyzed with each data set.

Sampling for mercury analysis followed ultra-clean sampling and handling protocols (Gill and Fitzgerald, 1987; Bloom, 1995) during the collection of field samples and analysis of samples at Frontier Geosciences. Borosilicate I-CHEM™ glass with teflon-lined caps were used and samples were preserved at 0°C until maintained under laboratory established conditions. All handling of samples in the laboratory was undertaken in a mercury free clean air bench. Ultra-clean mercury trace metal protocol was used including the use of rigorously cleaned and tested teflon equipment and sample bottles and pre-screened and laboratory purified reagents. Primary standards used in the laboratory were NIST certified

or traceable to NIST certified materials. Monomethyl mercury standards made from pure powder and calibrated for monomethyl mercury (MMHg) against NBS-3133 and cross-verified by daily analysis of NRCC DORM-2. EPA Method 1631 was used. Total mercury was determined by BrCl oxidation, SnCl₂ reduction, and dual gold amalgamation. All mercury analysis was performed using cold vapor atomic fluorescence (CVAFS) (Bloom et al., 1988). MMHg was liberated from water through distillation using an all teflon distillation system (Horvat et al., 1993). Distilled samples were analyzed using aqueous phase ethylation purging onto Carbotrap, isothermal GC separation, and CVAFS (Bloom, 1989). Laboratory analyses followed quality assurance measures with the following minimum frequency: the collection of laboratory duplicates (1 per 10 samples), method blanks (3 per analytical batch), filtration blank (1 per 10 samples), and laboratory-spike recovery (1 per 10 samples) or standard reference material (1 per 10 samples).

3. Geology and types of deposits

The Coast Range mercury mineral belt extends for 400 km along the Coast Range of California (Fig. 1) and contains 51 mercury deposits that have each produced in excess of 1000 flasks of mercury (a flask equals 76 lbs of mercury). Numerous smaller deposits, occurrences, and tracts of country rock with elevated concentrations of mercury are also present in the mineral belt. Production of mercury within the mineral belt began in the late 1840s and coincided with the California gold rush that included both placer and hard rock mining in the Sierra Nevada gold belt. Much of the 2.8 million flasks of mercury produced from the mineral belt was used in the amalgamation process to recover gold in the Sierra Nevada gold belt and precious metal mines in the adjacent state of Nevada. Production from mercury mines ended in the early 1970s because of the decrease in demand for mercury caused by environmental concerns. However, byproduct mercury continues to be produced from gold mining operations because environmental regulations

restrict the release of mercury from these mines. Many of the inactive mines currently pose environmental problems to watersheds, where fish and other biota have elevated levels of methylmercury which is derived from mercury mine wastes and mine drainage.

There are two types of mercury deposits in the California Coast Range mineral belt: silica-carbonate type, and hot-spring type (Rytuba, 1996). The silica-carbonate mercury deposits formed from low-temperature (<120°C) hydrothermal fluids and contain elevated levels of nickel, cobalt, chromium, and-zinc (Table 1) that reflect their close association with serpentinite (Rytuba and Kleinkopf, 1995). The deposits are localized along the contacts of serpentinite bodies and typically occur over a vertical interval of as much as 600 m. Hot-spring type mercury deposits formed in the near-surface environment, generally within 100 m of the surface, and commonly occur in and adjacent to volcanic centers (Rytuba, 1993). These deposits formed from low-temperature hydrothermal fluids composed primarily of meteoric water, and have a trace metal association of lithium, boron, arsenic, antimony, gold, and tungsten. In some mercury mining districts both deposit types are present, but the early formed silica-carbonate mineralization is always overprinted by younger hot-spring type mercury mineralization (Rytuba, 1996). In the northern part of the mercury mineral belt active hot springs are associated with some of the recently formed mercury deposits, and at some deposits the thermal springs are actively depositing mercury and associated metals (White, 1981; Donnelly-Nolan et al., 1993). Mine drainage from these deposits can be composed primarily of thermal water or a mixture of thermal and meteoric water (Rytuba, 1997).

4. Mining and processing methods for mercury ores

Individual mercury ore deposits are generally small in area, rarely exceeding more than 1 km², and the disturbed area around the deposits is similarly restricted. Silica-carbonate type mercury

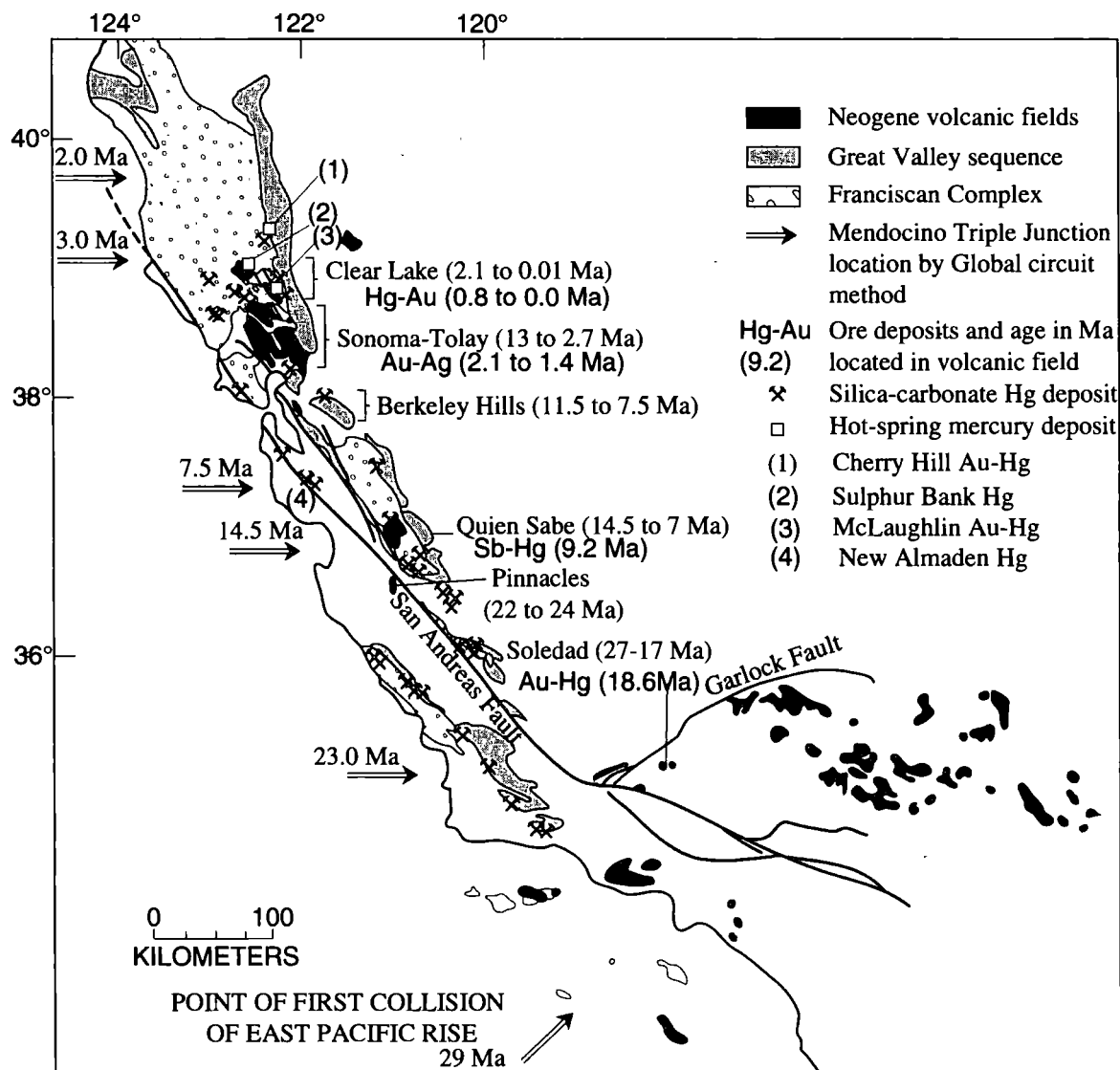


Fig. 1. Geologic map of mercury deposits and volcanic centers in the California Coast Range mercury mineral belt. The deposits developed in a slab window tectonic environment as the Mendocino Triple Junction migrated northward along the western part of California. Silica-carbonate type mercury deposits formed during the early phase of regional increase in the heat flow above the slab window and hot-spring mercury-gold deposits formed late in the evolution of the volcanic fields. Both deposit types become younger toward the north and active hot springs are associated with deposits in the northernmost part of mineral belt. Distribution of volcanic rocks modified from Johnson and O'Neil (1984).

deposits have been mined by underground methods because of the large vertical extent of these ores. Hot-spring type deposits occur over a more restricted vertical interval and have been mined by both open pit and underground methods. Only

a few mines have been exclusively open pit operations. Most of the large deposits have been underground operations with stope mining of ore shoots occurring over a vertical distance of a few hundred meters and up to 600 m at the largest

Table 1
Geologic and geochemical factors that control mine drainage composition

| | Silica-carbonate type mercury deposits | Hot-spring type mercury deposits |
|-----------------------|---|-------------------------------------|
| Trace metals | Ni–Co–Cr–Sb–Zn–Cu | Au–As–Sb–Li–W |
| Alteration | Carbonates-quartz | Adularia-quartz-clays |
| Sulfides | Pyrite-marcasite 5–50% | Pyrite 2–5% |
| Host rocks | Serpentinite-(shale) | Clastic rocks (volcanic) |
| Structural Control | Serpentinite contacts | Faults-volcanic vents |
| Ore minerals | Cinnabar (HgS)- elemental Hg | Cinnabar (HgS) |
| Secondary Minerals | Mercury sulfates- chlorides | Mercury sulfates- chlorides |

mines. Waste rock was often used to backfill underground workings and only a small fraction of waste rock was brought to the surface. Thus, ground water that infiltrated the extensive underground workings after mining ceased reacted with rock exposed along the walls of the mine workings, and with crushed waste rock containing variable amounts of iron sulfides and mercury.

The primary processing method for mercury ores consisted of heating ores to 600–700°C to volatilize mercury followed by a condensing process to recover liquid elemental mercury. Ores were typically processed at the mine site and only rarely sent to a central processing facility. Thus the amount of calcines present at the mine site reflects the amount of ore that was mined. Roasting of the ore resulted in the oxidation of iron sulfides causing the calcines to have a characteristic red color. The ores were processed in several types of retorts and furnaces. Furnaces differ from retorts in that furnaces internally heat the ores, mixing exhaust gases from the fuel with mercury vapor, and process a continuous feed of ore. Retorts consist of one or more pipes that contain a single charge of ore that is externally heated and vapors from the fuel do not mix with the volatilized mercury. Secondary mercury phases more readily formed in furnaces than in retorts. Retorts generally had a small capacity, approximately 500 lbs of ore per pipe, and were utilized at small mines having high-grade ore bodies. Thus, the volume of mine tailings generated was small but because of inherent inefficiency of retorts the

residual amount of mercury in the tailings was high, several hundred micrograms per gram. At the larger mines, retorts were utilized to purify sooty mercury recovered from the furnace condensing system. Furnaces that have been utilized include the Scott, Herreshoff, and several types of rotary furnaces having a capacity ranging from less than 10 to 350 tons/day. The most commonly used was the rotary furnace, which consists of a rotating, inclined iron cylinder into which ore is continuously fed and from which the calcine is removed. Mercury vapor and other gases are drawn from the upper end of the cylinder into a dust collector and then condenser before being released through a stack. This type of furnace generated large volumes of calcines that contained residual mercury generally ranging from approximately 20 to 150 µg/g. However, because the Scott furnace was generally built from brick, these furnaces were inefficient until considerable ore had been processed through them and the bricks had become saturated with elemental mercury. At the end of mining the bricks from the furnace were generally retorted to recover the mercury. Thus, calcines initially generated from a Scott furnace can contain very high residual mercury, from 500 to 1000 µg/g.

Condensing systems cool the vapor from the furnaces in order to separate the liquid mercury from other stack gases and range from simple single pipe to complex multiple pipe condensers. Condensing systems usually consist of pipes 8–15 inches in diameter and several hundred feet in

length that are bent into successive U shapes. The U-bends at the base of the condensing system are immersed in a water tank and each is equipped with a drain hole so that condensed mercury can be collected in the tank. Both air and water-cooled condensing systems have been utilized. In the more simple retorts the condensing system consists of an iron pipe 2–4 inches in diameter and 5–10 feet long sloping downward from the top of the retort to a collection tank. Approximately two-thirds of the product recovered from the condensers consist of elemental mercury and the remainder consists of a fine soot composed of rock dust, mercury sulfides and sulfates, fuel soot, water and finely dispersed elemental mercury. In older mines this material was dried on steam tables. Calcium carbonate was used to aid in the mechanical coagulation of finely condensed particles of mercury from soot and removed from the table through a small pipe leading to a collecting tank. Mercury was bottled near the retort or furnace site and inefficiencies in this process as well as other spillage has caused mercury contamination of soils and calcines.

5. Mercury mine drainage composition

The geology and geochemistry of the type of mercury deposit provides an important control on the composition of mercury mine drainage. Geologic factors (Table 1) such as mercury ore mineralogy, host rock composition, and amount of iron sulfides present are important in determining the pH, metal, and anion concentrations in mine drainage. The physical and chemical parameters of mine drainage from several mercury deposits representative of the two types of mercury deposits present in the California Coast Range mercury mineral belt are summarized in Table 2. The mine drainage composition data reflect three different mine environments: (1) water at the point of discharge from mine workings; (2) water that has reacted with calcines; and (3) mine drainage that has mixed with stream water. The composi-

tion of mine drainage is discussed in these three different mine environments because the concentration of mercury species in mine drainage is strongly affected by atmospheric oxygen and reaction with calcines after it is discharged from the mine workings.

5.1. Mine drainage composition at the point of discharge from mine workings

Mine drainage at the point of discharge from mine workings from silica-carbonate type mercury deposits is moderate to weakly acidic with pH ranging from 3.1 to 6.9. Pyrite and marcasite are the primary acid-generating sulfides in these deposits and comprise from 2 to 10 vol.%. Because of the buffering capacity of serpentinite host rocks and the carbonate hydrothermal alteration minerals associated with this deposit type, the pH of mine drainage is typically not extremely low. Hot-spring type mercury deposits are hosted by a variety of rock types having varying degrees of buffering capacity so the pH of mine drainage from this mercury deposit type is variable. Low pH is associated with deposits hosted in elastic rocks, or volcanic rocks that have been intensely altered. The trace metals present in mine drainage associated with silica-carbonate type deposits reflect the serpentinite host rock of these deposits and consist of moderate to high concentrations of nickel, cobalt, chrome, antimony, zinc, and copper (Rytuba and Kleinkopf, 1995). Mine drainage from hot-spring type mercury deposits contain low to moderate concentrations of antimony, arsenic, lithium, and tungsten (Rytuba, 1997).

The iron concentration of mine drainage ranges from 0.1 to 7600 mg/l (Table 2). The highest iron concentrations are associated with silica-carbonate type deposits that are localized in and adjacent to mafic intrusions where large amounts of pyrite and marcasite, up to 50% by volume, were introduced into the country rock. Mine drainage waters from hot-spring type deposits have lower concentrations of iron because the deposits have lower iron sulfide content (Table 2).

Table 2

Chemistry of mercury mine drainage from silica-carbonate and hot-spring type deposits

| | Sulfate (mg/l) | Total Hg (µg/l) | Filtered Hg (µg/l) | Total MMeHg (ng/l) | Filtered MMeHg (ng/l) | Fe total (mg/l) | Fe ²⁺ (mg/l) | pH |
|---|-------------------|--------------------|-----------------------|--------------------------|-----------------------------|--------------------|----------------------------|------|
| <i>Mercury mine drainage composition at point of discharge</i> | | | | | | | | |
| <i>Silica-carbonate type</i> | | | | | | | | |
| BV1 | 3900 | 0.01 | 0.001 | 0.04 | 0.03 | 7600 | 7600 | 4.8 |
| BV4 | 3300 | 0.05 | 0.001 | 0.64 | 0.32 | 2.8 | 0.9 | 6.9 |
| KLW2 | 3700 | 8.00 | 3.7 | 1.1 | 0.9 | 150 | 150 | 3.1 |
| KNW1b-RA | 5500 | 3.03 | 3.0 | 0.66 | 0.35 | 140 | 130 | 6.0 |
| 98KN10 | 12000 | 2.20 | 0.77 | 1.26 | 0.39 | 350 | 340 | 5.6 |
| CRW1b-RA | 640 | 0.01 | 0.003 | 0.12 | 0.08 | 71 | 71 | 5.9 |
| 97CRb-1W | 550 | 0.04 | 0.013 | 0.05 | 0.05 | 59 | 48 | 3.9 |
| 97CR-2W | 530 | 0.005 | 0.005 | 0.05 | 0.03 | 200 | 200 | 5.5 |
| NIM1 | 3900 | 0.2 | | | | 490 | 490 | 4.7 |
| R97-1W RA | 1000 | 0.002 | 0.0003 | < 0.003 | < 0.003 | 180 | 47 | 6.5 |
| 97-H1A | 760 | 0.006 | 0.002 | 0.07 | 0.03 | 16 | 16 | 6.5 |
| 98SM-1W | 320 | 0.019 | 0.0002 | 0.04 | 0.02 | 7.7 | 5 | 6.2 |
| 97TP1W | 2.7 | 0.069 | 0.04 | 0.06 | 0.05 | 26 | 23 | 4.9 |
| <i>Hot-spring type</i> | | | | | | | | |
| M2 | 3300 | 0.047 | | < 0.2 | | 1.7 | 1.7 | 7.2 |
| MPW6-RA | 6700 | 0.18 | 0.05 | 0.03 | 0.01 | 8.5 | 0.4 | 7.5 |
| 97TR 1w | 2020 | 0.01 | 0.001 | 0.005 | 0.003 | 0.5 | 0.0 | 6.6 |
| 97TRb 1w | 1760 | 0.03 | 0.005 | 0.009 | 0.002 | 0.1 | 0.0 | 6.6 |
| Elgin 2 | 90 | 11 | | | | 0.1 | 0.1 | 8.1 |
| 97SB-1W | 2580 | 0.70 | 0.65 | 0.52 | 0.32 | 30.0 | 11 | 3.0 |
| 98HS-1W | 180 | 0.21 | 0.0007 | 0.06 | 0.017 | 2.0 | 0.8 | 6.4 |
| <i>Mercury mine drainage composition after reaction with mine tailings and wastes</i> | | | | | | | | |
| <i>Silica-carbonate type</i> | | | | | | | | |
| MDW2 | 7700 | 43 | 39 | 8.9 | 5.05 | 490 | 490 | 5.0 |
| MDW8 | 27000 | 270 | 280 | 47 | 21.9 | 610 | 3.1 | 2.5 |
| BV2 | 16000 | 240 | 2.4 | 0.09 | 0.06 | 1080 | 500 | 3.0 |
| BV3 | 33000 | 450 | 10 | 0.07 | 0.04 | 1700 | 480 | 2.6 |
| <i>Hot-spring type</i> | | | | | | | | |
| 97TR 2 | 2000 | 2.1 | 1.04 | 0.44 | 0.121 | 0.40 | 0.0 | 8.1 |
| 97TR b2 | 1850 | 2.6 | 0.87 | 1.21 | 0.39 | 0.29 | 0.02 | 8.3 |
| <i>Mercury mine drainage composition after mixing with stream water</i> | | | | | | | | |
| <i>Silica-carbonate type</i> | | | | | | | | |
| 97NI-5W | 4390 | 17.2 | 16.22 | 2.37 | 2.3 | 10.9 | 480 | 3.8 |
| 97NI-6W | 2150 | 11.9 | 2.727 | 4.50 | 5.3 | 6.9 | 29 | 6.2 |
| 97NI-4W | 2500 | 13.5 | 1.865 | 3.56 | 1.1 | 6.4 | 23 | 5.9 |
| 97NI-3W | 2480 | 13.5 | 3.275 | 3.35 | 0.47 | 6.7 | 24 | 6.0 |
| 97NI-2W | 2550 | 10.1 | 0.73 | 1.69 | 0.18 | 3.4 | 0.0 | 7.9 |
| 97NI-1W | 2060 | 19.6 | 0.12 | 2.47 | 0.03 | 2.2 | 0.0 | 8.2 |
| <i>Hot-spring type</i> | | | | | | | | |
| TR974W | 1000 | 1.4 | 0.45 | 0.96 | 0.046 | 0.41 | 0 | 8.18 |

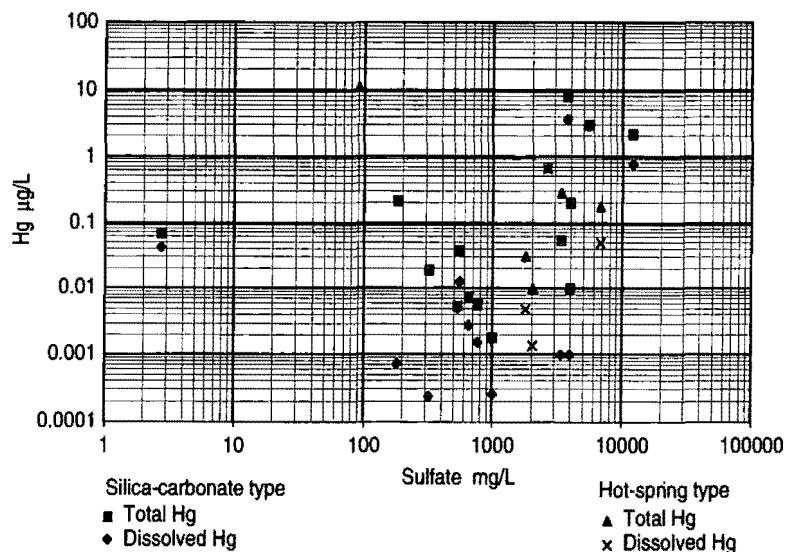


Fig. 2. Total and dissolved mercury concentration vs. sulfate concentration in mine drainage at the point of discharge from mine workings.

In both cases iron is present dominantly in the reduced form, Fe(II), and for many of the mine drainages sampled it is nearly equivalent to the total iron concentration. Total mercury concentration in mine drainage from silica-carbonate type deposits ranges from 0.005 to 8.0 µg/l and from hot-spring type deposits it ranges from 0.01 to 0.70 µg/l (Table 2, Fig. 2). Filtered samples (0.45 µm) of mine drainage typically have lower concentrations of mercury for both deposit types indicating that a significant portion of the mercury present is adsorbed onto particulate phases and colloids (Fig. 2). Sulfate concentration of mine drainage is commonly high for both deposit types, typically exceeding several thousand milligrams per liter (Table 2). Oxidation and weathering of iron sulfides exposed in underground mine workings and back fill waste rock contribute sulfate to the mine waters. The highest sulfate concentrations are associated with silica-carbonate type mercury deposits that have a high iron sulfide content. Total methylmercury concentration of mine drainage ranges from <0.003 to 1.26 ng/l with highest concentrations associated with silica-carbonate type deposits (Fig. 3). Filtered samples of mine drainage typically contain lower

concentration of methylmercury indicating that methylmercury present is also adsorbed onto particulate phases and colloids (see discussion below). Highest methylmercury concentrations occur in waters with high sulfate concentration indicating that underground mines provide a favorable environment for sulfate reducing bacteria to methylate mercury. However, the methylation of mercury is likely limited by the amount of dissolved organic carbon in the underground mine environment.

5.2. Mine drainage composition after reaction with atmospheric oxygen and mine wastes

After mine drainage exits the underground mine workings, reaction of the water with atmospheric oxygen results in the oxidation of the dissolved iron(II) to iron(III) and precipitation of iron oxyhydroxide, which is characteristic of most mercury mine drainage. Mine drainage from silica-carbonate type deposits that have high iron concentration can develop extreme acidity (pH as low as 2.6) after reaction with atmospheric oxygen causes precipitation of iron oxyhydroxide. Mine drainage waters from hot-spring type deposits are

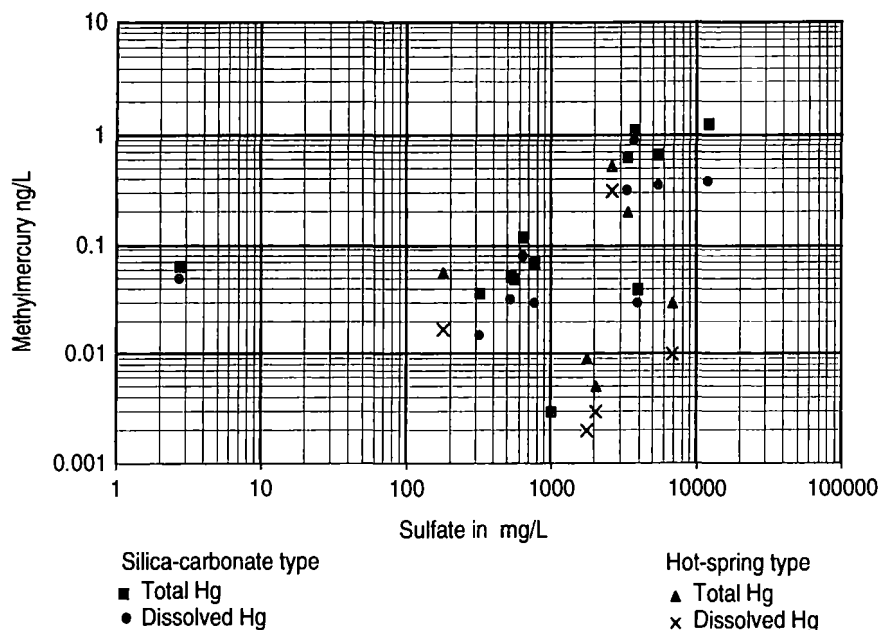


Fig. 3. Total and dissolved methylmercury concentration vs. sulfate concentration in mine drainage at the point of discharge from mine workings.

typically weakly acidic because thermal waters having a high alkalinity (Donnelly-Nolan et al., 1993) commonly mix with the mine drainage. In some cases mine drainage is composed dominantly of thermal water, such as at the Elgin mine, where the pH is alkaline, 8.15 (Table 2).

Mine drainage commonly reacts with mine wastes that were deposited at the mine site. After exiting the mine underground workings, mine drainage often flows over and through mercury enriched calcines or waste rock because this material was typically disposed of in and adjacent to a stream channel that was closest to the mine workings. Mine tailings contain significant concentrations of mercury, up to several 100 $\mu\text{g/g}$ (Rytuba, 1997) and the mercury is commonly present in soluble phases such as mercury sulfates and oxy-chlorides that were formed during the ore roasting process (Kim et al., 1998). As mine drainage reacts with calcines, mercury and methylmercury concentrations in the water increase dramatically because soluble mercury phases are dissolved, and the addition of sulfate to the calcines allows sulfate-reducing bacteria to methyl-

ate the dissolved mercury (Table 2). At the Turkey Run mine, mine drainage as it exits the underground mine workings has relatively low concentrations of total and dissolved mercury, 0.032 and 0.005 $\mu\text{g/l}$, and total and dissolved methylmercury, 0.009 and 0.002 ng/l (Fig. 4; 97TR samples, Fig. 2). After flowing through and reacting with mine tailings, the concentrations of mercury and methylmercury increase by approximately two orders of magnitude. Total and dissolved mercury increases to 2.6 and 0.87 $\mu\text{g/l}$, respectively, and the total and dissolved methylmercury increases to 1.2 and 0.39 ng/l. Because the mine drainage has a high sulfate content, 2020 mg/l, the addition of sulfate to the calcines enhances the ability of sulfate-reducing bacteria to methylate mercury that is dissolved from the mine tailings. Mercury contaminated soils, especially those that are saturated with water, have been shown to provide a favorable environment for methylation of mercury (Hines et al., 1999). The saturation of mine wastes by mine drainage having a high sulfate concentration provides an especially favorable environment for the methylation of mercury.

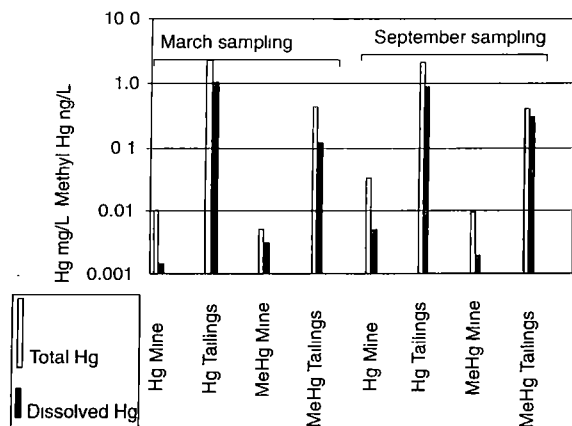


Fig. 4. Mercury and methylmercury concentration in mine drainage at the point of discharge from mine workings, and after flowing through and reacting with mine tailings at the Turkey Run mine for two sampling periods.

6. Methyl mercury formation and adsorption in streams impacted by mine drainage

6.1. Methylation of mercury and adsorption onto iron oxyhydroxide

Streams impacted by mercury mine drainage have elevated levels of mercury and associated metals, anions such as sulfate, low pH, and stream beds that are coated by iron oxyhydroxides. Because of the high concentration of sulfate and mercury, these streams provide a favorable environment for sulfate reducing bacteria to methylate mercury (Rytuba, 1997). Total concentrations of methylmercury in stream waters impacted by mercury mine drainage commonly are several nanograms per liter (Table 2). Methylmercury concentrations are higher than those present in the mine drainage at the point of discharge from the mine workings, and similar to the concentration in mine drainage that has reacted with mine tailings. Thus methylation of mercury occurs in all three mine environments where mine drainage is present.

As mercury mine drainage mixes with oxygenated stream waters dissolved iron(II) is oxidized to iron(III) and precipitated as iron oxyhydroxide. Iron oxyhydroxide commonly accumulates on the surface of the streambed as a

several-centimeters-thick floc. Mercury and methylmercury adsorption onto iron oxyhydroxide substrate is an important process that controls the concentration of mercury species in streams impacted by mercury mine drainage. In order to document the degree of adsorption of mercury species onto iron oxyhydroxides, water and coexisting iron oxyhydroxides were sampled from several streams impacted by mercury mine drainage and analyzed for both total mercury and methylmercury. The concentrations of total mercury and methylmercury in iron oxyhydroxide and in the coexisting water are shown in Figs. 5 and 6 as a function of pH. Mercury is strongly adsorbed by iron oxyhydroxide over the pH range of 3.2–7.1 with concentrations as high 220 $\mu\text{g/g}$. The concentration of mercury in the iron oxyhydroxide substrate is typically one, but as much as three, orders of magnitude greater than that in the coexisting water. Above pH 7.1 mercury adsorption is less effective and the concentration of mercury in the water exceeds that in the iron oxyhydroxide. Macroscopic experiments have demonstrated that the sorptive behavior of mercury(II) onto goethite exhibits a gradual decrease with increasing pH after reaching a maximum adsorption at neutral pH (Barrow and Cox, 1992). This pattern is reflected in these natural samples. Methylmercury is also strongly adsorbed by iron oxyhydroxide over the pH range 3.2–7.1 with up to 105 ng/g of methylmercury concentrated in iron oxyhydroxide. The concentration of methylmercury in the iron oxyhydroxide substrate is typically one, but as much as two, orders of magnitude greater than that in the coexisting water. Above pH 7.1, methylmercury concentration in the coexisting water approaches the concentration in iron oxyhydroxide indicating that adsorption is less effective at higher pH. Methylmercury forms sulfate, chloride, and hydroxide complexes. Experimental studies demonstrate that in waters with moderate to high sulfate concentration the negatively charged sulfate complex, $\text{CH}_3\text{HgSO}_4^-$, predominates at low pH, and the neutral hydroxide complex predominates in alkaline waters (Sanz et al., 1999). The natural iron oxyhydroxide samples occur in waters with high sulfate concentrations. The negatively charged

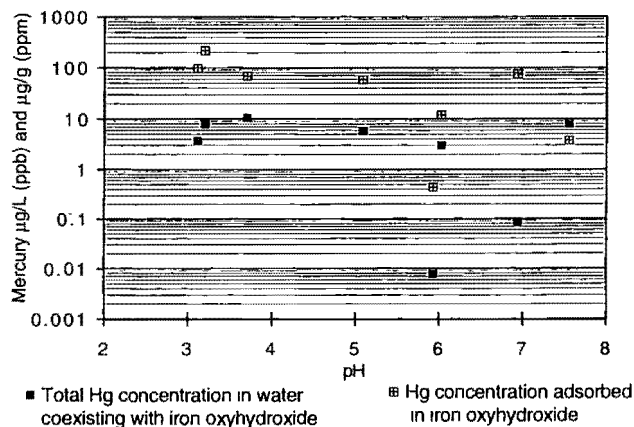


Fig. 5. Mercury concentration as a function of pH in water ($\mu\text{g/L}$) and sorbed onto coexisting iron oxyhydroxide ($\mu\text{g/g}$, ppm, dry wt. basis) that was precipitated in San Carlos Creek, a stream impacted by mercury mine drainage.

methylmercury sulfate complex is more effectively adsorbed by iron oxyhydroxide in low pH stream waters than is the neutral methylmercury hydroxide species that is the predominant species in alkaline waters. The distribution coefficient, K_d in liters per kilogram, for both mercury and methylmercury with respect to iron oxyhydroxide (Fig. 7) significantly decreases at pH above 7.1.

6.2. Mercury and methylmercury fate and transport in streams impacted by mine drainage

The methylation of mercury and the adsorption of mercury and methylmercury onto iron oxyhy-

droxides are important processes in controlling the fate and transport of mercury species in streams impacted by mercury mine drainage. These processes are well demonstrated in San Carlos Creek, a stream that is strongly impacted by the release of untreated mine drainage from the underground workings of the New Idria mine, the second largest mercury mine in the central part of the California mercury mineral belt. Since its closure in the 1980s mine drainage from the extensive underground workings has flowed through mine wastes and calcines before entering San Carlos Creek where it mixes with oxygenated waters and precipitates large amounts of iron

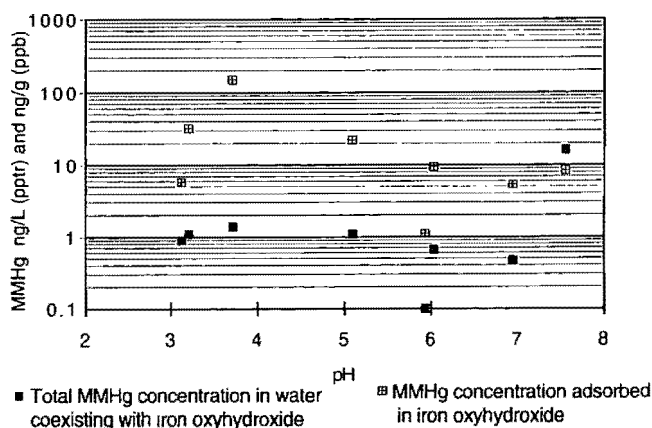


Fig. 6. Methylmercury concentration as a function of pH in water (ng/L) and sorbed onto coexisting iron oxyhydroxide (ng/g, ppb, dry wt. basis) that was precipitated in San Carlos Creek, a stream impacted by mercury mine drainage.

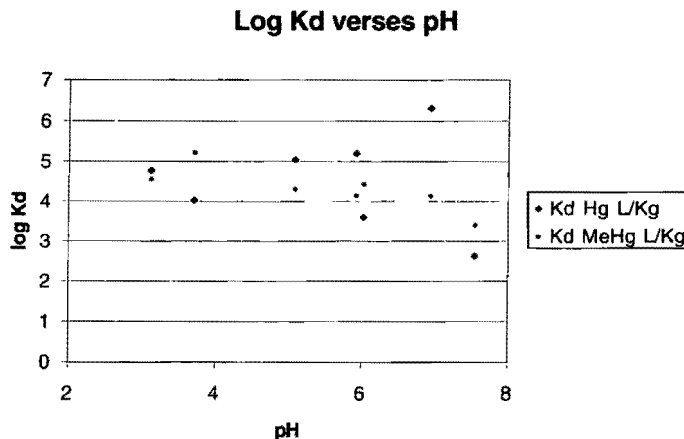


Fig. 7. Distribution coefficient, $\log K_d$ in liters per kilogram, for mercury and methylmercury with respect to iron oxyhydroxide as a function of pH.

oxyhydroxide. The creek water has a red color due to the large component of suspended iron oxyhydroxide and the streambed is coated with this phase for several tens of kilometers downstream from the mine. Mine drainage as it exits the mine workings has a relatively low mercury concentration of $0.2 \mu\text{g/l}$ and high iron(II), 490 mg/l , and sulfate, 3900 mg/l . After the mine

drainage flows through and reacts with mine wastes and calcines total mercury concentration increases to $18 \mu\text{g/l}$ and is present predominantly in the dissolved fraction (Fig. 8). Addition of sulfate to the mine wastes by the mine drainage causes methylation of mercury within the saturated mine wastes. Methylmercury concentration of the mine drainage increases to 2.4 ng/l and is

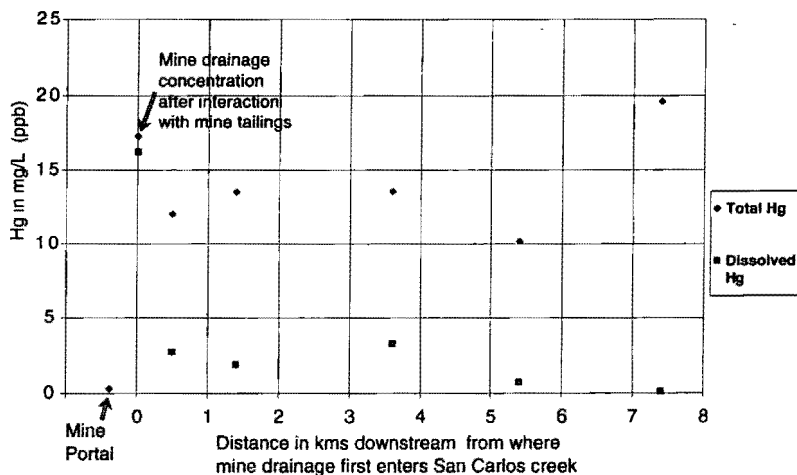


Fig. 8. Total and dissolved mercury concentration in mine drainage and waters of San Carlos Creek that are impacted by mine drainage as a function of distance from where the mine drainage first exits the underground mine workings, site at -0.5 km . Mine drainage interacts with mine wastes and tailings at 0 km and enters and mixes with the oxygenated waters of San Carlos Creek at 0.5 km . Data points from 0.5 to 7.5 km are from San Carlos Creek that is strongly impacted by mine drainage and has a red color from the copious amounts of iron oxyhydroxide in the creek water and stream bed.

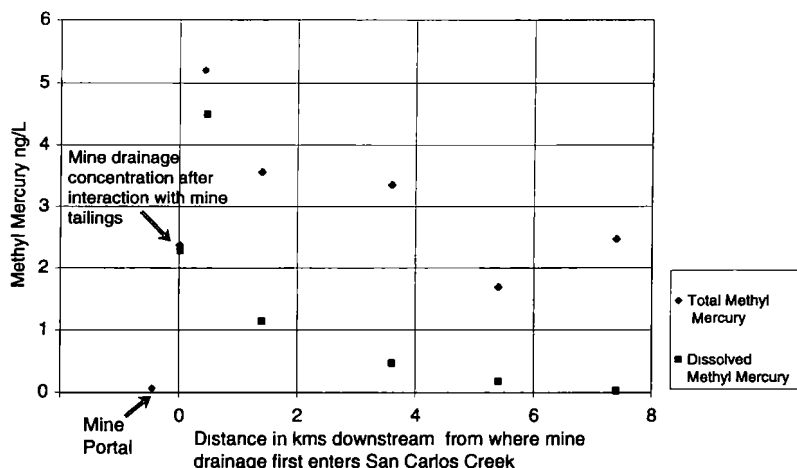


Fig. 9. Total and dissolved methylmercury concentration in mine drainage and waters of San Carlos Creek that are impacted by mine drainage as a function of distance from where the mine drainage first exits the underground mine workings, site at -0.5 km. Mine drainage interacts with mine wastes and tailings at 0 km and enters and mixes with the oxygenated waters of San Carlos Creek at 0.5 km. Data points from 0.5 to 7.5 km are from San Carlos Creek that is strongly impacted by mine drainage and has a red color from the copious amounts of iron oxyhydroxide in the creek water and stream bed

present predominantly in the dissolved fraction (Fig. 9) because iron(II) predominates. As the mine drainage enters and mixes with the oxygenated waters of San Carlos Creek, iron is oxidized and precipitated as an iron oxyhydroxide floc that is present in the water column and as a coating on the streambed. Although total mercury concentration remains high, $12 \mu\text{g/l}$, the dissolved component decreases because of adsorption of mercury onto iron oxyhydroxides suspended within the water column. As the mine drainage water continues to mix with the stream water, and iron(II) is completely oxidized and precipitated as iron oxyhydroxide, the dissolved component of mercury is reduced. At a distance of 7.5 km downstream from the mine, dissolved mercury component is completely removed by adsorption (Fig. 8). Transport of mercury in the stream is primarily as a particulate phase and the total concentration of mercury reflects the amount of iron oxyhydroxide present in the water. Both total and dissolved methylmercury increases after mine drainage initially enters San Carlos Creek (Fig. 9) indicating that methylation of mercury continues to occur in this environment as the mine drainage initially mixes with the stream water. However, as the mine drainage continues

to mix with stream water, the dissolved component of methylmercury is reduced by adsorption onto iron oxyhydroxide to a very low level, 0.003 ng/l , at a distance of 7.5 km downstream from the mine (Fig. 9). Transport of methylmercury in the lower reaches of the stream is dominantly in the particulate phase and the total concentration is a function of the amount of iron oxyhydroxide in the water column.

7. Conclusions

Mercury mine drainage poses a significant environmental problem because it has elevated levels of mercury and methylmercury as well as high concentrations of sulfate. The sulfate in mine drainage enhances methylation of mercury by sulfate reducing bacteria in calcines and mine wastes saturated by mine drainage and where mine drainage first mixes with stream water. Low to moderate concentration of mercury and methylmercury are present in mine drainage when these waters initially exit the mine workings. Both mercury and methylmercury concentration increase substantially in mine drainage as the water flows through and reacts with calcines and waste rock.

This commonly occurs at many mercury mines because calcines and waste rock were typically disposed of in a stream channel closest to the mine workings with the expectation that erosion would redistribute this material downstream, thus creating space for additional mine wastes. Mine drainage dissolves the more soluble mercury phases present in the calcines and waste rock and introduces sulfate which enhances methylation of mercury in the saturated mine wastes. Thus, mine drainage after it reacts with mine wastes typically has much higher concentrations of mercury and methylmercury than when it first exits from the underground mine workings. Remediation at mercury mines that have a mine drainage problem should address the diversion of the mine drainage so that it does not react with calcines or mine wastes. This simple measure will decrease methylation in the mine wastes and minimize the release of mercury and methylmercury.

Where mercury mine drainage initially enters a stream enriched in dissolved organic carbon, the addition of mercury and sulfate provides an environment for methylation of mercury. As the mine drainage mixes with oxygenated stream waters, oxidation of iron(II) causes precipitation of iron oxyhydroxide and this phase effectively adsorbs both mercury and methylmercury. As a result of adsorption, the dissolved component of both these mercury species decreases downstream from the mine site and mercury species are transported primarily in the particulate phase. In the Mediterranean climate of the California Coast Range where the summer months essentially have no rain, iron oxyhydroxides accumulate in the bed load of streams impacted by mercury mine drainage. Because stream flow is low and non-turbulent, both dissolved mercury and methylmercury are removed from the stream water by adsorption onto iron oxyhydroxide and transport of mercury species from the mine site is relatively low. During the first high flow events in autumn, iron oxyhydroxide floc that is enriched in mercury and methylmercury is seasonally flushed and distributed downstream. Both mercury and methylmercury enriched iron oxyhydroxide enter larger water bodies during this high flow event and become available to biota, such as zooplankton,

in the lower part of the food web (Kainz et al., 1999). Mercury mines that release mine drainage can generate very high concentrations of iron-rich mercury-bearing precipitates that can be significant source for both bioavailable mercury and methylmercury entering reservoirs or lakes.

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